Chemical Physics Letters 587 (2013) 40–44

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Surface plasmon response of metal spherical nanoshells coated with dielectric overlayer

Peihong Cheng [a,*], Jilong Bao [a], Ligang Wu [a], Xue Li [c], Hongxia Zhao [a], Renxiang Zhu [a], Jinxia Wang [a], Dongsheng Li [b]

[a] *School of Electronic and Information Engineering, Ningbo University of Technology, Ningbo 315016, People's Republic of China*
[b] *State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*
[c] *Key Laboratory of Infrared Imaging Materials and Devices, Shanghai Institute of Technical Physics, Chinese Academy of Science, Shanghai 200083, People's Republic of China*

ARTICLE INFO

Article history:
Received 5 May 2013
In final form 18 September 2013
Available online 25 September 2013

ABSTRACT

Surface Plasmon Resonance (SPR) characteristics of metal spherical nanoshells coated with different dielectric overlayers were investigated in this Letter. Besides band position, it is found that the line width of the symmetric dipole SP resonance is affected by the overlayer coating when the coupling strength of the inner surface cavity mode and outer surface sphere mode is strong. When the surrounding dielectric constant is comparative to that of core silica, narrowest damping width is expected. The computation results also demonstrate that the quality factors and electromagnetic field distribution are dependent on the overlayer coating. Consequently, an appropriate dielectric overlayer coating may be an important way of tuning SP characteristics of metal nanoshells.

1. Introduction

Surface plasmon (SP) in noble nanostructures has found great potential applications in optical sensing, medical imaging, and biologic detection due to tunable SP resonance by varying the shape, structure, and local environment of nanostructures [1]. Metal nanoshells, which consisting of a dielectric core and a metallic shell, exhibit attractive features due to the hybridization of the plasmons supported by the nanoscale sphere and a cavity in the surrounding medium. The SP resonance exhibits wide-range tunability through the UV to IR with varying the radius ratio between core and shell. Additionally, its radiative efficiency is much higher compared with that of compact metal nanoparticles of the same size. All these remarkable properties of the metal nanoshell make it promising in various kinds of optoelectronic field [2,3].

A significant amount of works have been done on the investigation of SP characteristics of metal nanoshells. Besides core and shell radius, the dielectric properties of the surrounding environment were also found affecting the SP resonance band [3–6]. Increasing the dielectric constant of the surrounding can tune the absorption band linearly, which is also the physics basis for the sensing application. Under certain circumstance, a dielectric overlayer coating is indispensable, such as surface decoration in imaging and sensing field [2]. Moreover, the overlayer on metal nanoparticles can protect metal surface from photochemical degradation by absorbed species. Several groups [7–12] have prepared protected Ag surfaces by coating metal islands with dielectric medium such as SiO_x, TiO_2 and other oxide, and the role of this overlay in tuning SPR has been paid attention. Theoretical works have also been done on layered plasmonic nanopheres. Qiu et al. used an EM analysis method to compute the light scattering by coated spheres with radial dielectric and magenetic anisotropy [13]. They found that one may make the anisotropic coated particle scattering extraordinarily or transparent by judicious pairing of plasmonic materials and control of core–shell radius ratio [14,15].

In this Letter, we focused on SP characteristics of metal nanoshells with dielectric medium coated as an overlayer. The influences of the thickness and refractive index of the overlayer on the SP resonance properties, including band positions, bandwidths, quality factors and electromagnetic fields were investigated theoretically in detail. The simulation results show that SPR bands can be tuned and the quality factors can be improved by appropriately dielectric overlayer coating. The SP band tunablility and high E-field inside the core–shell with an appropriate coating may be applicable in sensing or SP cavity mode based microlaser [16].

2. Theoretical modeling

The geometry of the overlayer coated nanoshells is illustrated schematically in the inset of Figure 1. Inner and outer radii of r_1, r_2 are used to characterize the size of the core–shell, which is denoted as $[r_1, r_2]$ in this Letter. Finite difference time domain (FDTD) method was used in the numerical computation of extinction efficiency and electromagnetic field of the metal nanoshell. The core material and metal was selected as silica and Ag respectively,

---

* Corresponding author.
E-mail address: peihongcheng@163.com (P. Cheng).

0009-2614/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cplett.2013.09.046

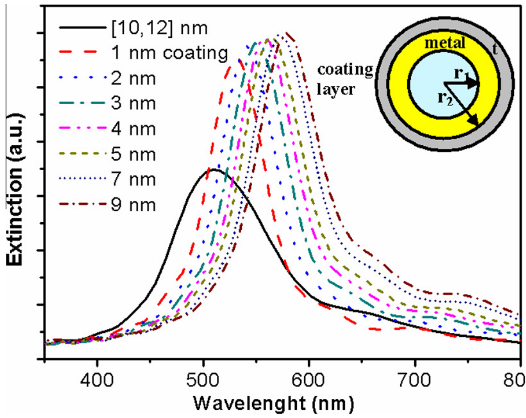

Figure 1. Extinction spectra of [10,12] nm Ag nanoshell coated with silica of varying thickness, inset: schematics of overlayer coated Ag nanoshell. r_1, r_2: Inner and outer radius of the nanoshell; t: thickness of the coating layer.

and the refractive indexes used in the computation were theoretical fitting results using Lorentz–Drude model to the experimental values from Ref. [17]. The thickness t and refractive index n_c of the overlayer are varied to study the evolution of the SP characteristics, including SP resonance band position and full-widths at half-maximum (FWHM) of Ag nanoshells coated with dielectric overlayer.

3. Results and discussion

Figure 1 shows the extinction spectra of [10,12] nm Ag nanoshells with and without overlayer coating. In this simulation, coating material is selected as silica, the same as the core material, and the overlayer thickness t is varied from 1 to 9 nm. Symmetric dipole oscillation modes due to hybridization of the inner cavity and outer sphere modes, were observed in all the extinction spectra [5,6]. As illustrated, the influence of overlayer on the symmetric mode at 488 nm is particularly pronounced. It is due to that a symmetric bonding mode has a large admixture of the surface plasmon on the outer surface (sphere plasmon), which is more sensitive to the embedding medium [4]. In particular, after 1–2 nm overlayer coating, the band redshifts and the intensity increase abruptly. When the overlayer thickness is further increased, however, the band intensity changes slightly but red-shifts gradually.

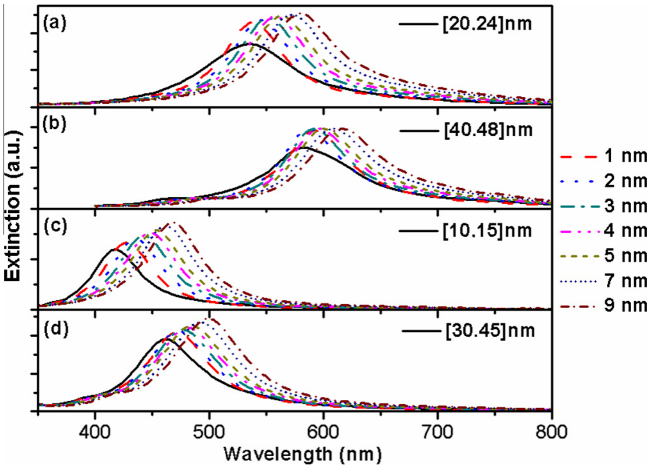

Figure 2. Extinction spectra of different size Ag nanoshell coated with silica of varying thickness. (a) [20,24] nm, (b) [40,48] nm, (c) [10,15] nm, and (d) [30,45] nm.

The effects of the overlayer on Ag nanoshells with different radius ratio r_1/r_2 and sphere volume were also studied. Figure 2a and b shows the extinction spectra of [20,24] and [40,48] nm Ag nanoshell with r_1/r_2 kept at 0.83, respectively. Figure 2c and d separately present the extinction spectra of [10,15] and [30,45] nm Ag nanoshell with $r_1/r_2 = 0.67$. Obviously, for the bare Ag nanoshells with equal radius ratio, the dipole mode redshifts with the increase of the core radius r_1. With r_1 kept as a constant, the dipole mode blueshifts as r_1/r_2 is increased. This observation is in accordance with the reported experiment results [3,18]. As demonstrated, the dielectric overlayer coating causes a redshift of the resonant band for all the nanoshells, even though the thickness is only 1 nm. The redshift can be explained in terms of overlayer coating induced surrounding dielectric constant increasing. Surrounding medium polarizes in response to the plasmon field, effectively reducing the strength of the surface charge and leading to a decreased restoring force and, consequently, lowering the plasmon energies [5]. In the case of the medium with higher dielectric constants, the screening effect is more pronounced. For the overlayer coated nanoshell, the surrounding dielectric constant $\bar{\epsilon}$ can be regarded as an average of the dielectric constants of coating overlayer ϵ_c and external atmosphere. Apparently, with the increase of the overlayer thickness, the average dielectric constant $\bar{\epsilon}$ is raised, leading to the linear redshift of the SP band.

Figure 3a compares FWHMs of the Ag nanoshells with varying overlayer thicknesses in Figure 2. Apart from r_1/r_2 of 0.83 and 0.67, the spectral behavior of Ag nanoshell with $r_1/r_2 = 0.5$ was also included. It is observed that the FWHMs change behavior is dependent on r_1/r_2. For the case of $r_1/r_2 = 0.83$, the FWHMs all exhibit a decrease at first after coating and then a slow increase by raising the overlayer thickness further. A minimum values were found at about 2 nm thickness. For r_1/r_2 of 0.67 and 0.83, the FWHMs all exhibit a slight broadening with the increase of the coating thickness. It is noted that modeling solid dielectric objects is done using the staircase approximation in FDTD method [19], so for structures of small size, errors may appear when grid size is not fine enough. However, errors induced abnormal spectra characteristics become negligible for structure with big r_1 and r_1/r_2. So the change behavior shown in Figure 3 cannot be ascribed to the computation errors.

To understand the effect of overlayer on the SPR characteristics in depth, the refractive index of the overlayer was also varied while the thickness was kept at 2 nm. As expected, the SP resonance band redshift due to the increase of the refractive indexes of the overlayer (not shown here). However, it is intriguing that the FWHMs also show different change behaviors for Ag nanoshells with varying radius ratio. Figure 3b presents the FWHMs of Ag nanoshells as a function of the refractive indexes. As shown, for nanoshells with $r_1/r_2 = 0.83$, the FWHMs decrease at first and demonstrate a minimum value when the refractive index is between 1.5 and 2.0. Further increasing the refractive indexes of the overlayer causes a slight linear broadening of the linewidth. However, the dependence of FWHMs on the refractive index of the coating layer is slight for the nanoshells with the radius ratios of 0.67 and 0.5.

The effect of the dielectric overlayer is similar to the effect of immersion in a medium with the same dielectric constant. Width broadening induced by surrounding dielectric index increasing has been observed experimentally and also been investigated theoretically [4–8]. It was interpreted that larger dielectric constant induces more intense perpendicular local field relative to incident electric field direction, and thus the scattering of the perpendicular direction moving electron results in a loss of electron phase coherence, leading to the broadening of the plasmon band [5]. Our results on nanoshells with small r_1/r_2 indeed demonstrate linewidth broadening with increased $\bar{\epsilon}$ by raising the coating thickness. However, there is a linewidth narrowing behavior for Ag